To study stability constants and thermodynamic properties of complexation of Paracetamol with Co$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ by PH metrically

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ABSTRACT
The equilibrium constants for metal complex formation have been employed from long as an effective measure and parameter of the affinity of a ligand for a metal ion in solution. PHmetry is one of the most convenient and successful technique employed for metal complex equilibrium measurements. pHmetric measurement of hydrogen ion concentration may be employed when the degree of complex formation is sensitive to the hydrogen ion concentration. Thus the degree of complex formation undergoes increase/decrease with change in pH. In the present work, we investigate the stability constants of Paracetamol complexes with Co$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$pHmetrically using pH metric technique at three temperatures (25 ±0.1, 30 ±0.1 and 35 ±0.1°C) and at an ionic strength of 0.1 mol L$^{-1}$ (KNO$_3$). The method of Calvin and Bjerrum as adopted by Irving and Rossotti has been employed to determine log K values. The thermodynamic parameters ΔG, ΔH and ΔS are calculated. System tend to progress in the direction of increasing entropy as entropy is a measure of a system’s tendency towards spontaneous change.

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ionic strength of 0.1 mol L\(^{-1}\) (KNO\(_3\)). The pH meter was calibrated with suitable buffers before use.

**a) Calvin – Bjerrum Titration**

The experimental procedure involved pHmetric titration of,

i) Free acid (0.01M) titration,

ii) Free acid (0.01 M) and ligand (0.05M) titration.

iii) Free acid (0.01M), ligand (0.05M) and metal ion (0.01M) against std. NaOH solution.

The dissociation of H\(^+\) between acid curve from ligand curve for the systems showed about pH 3.0 and then increase up to pH 12.0. The deviation at 0.1 M ionic strength pH 3.5, It indicate the commencement of complex formation.

**Method for determination of stability constants**

The dissociation constants of paracetamol was determined at 0.1 M ionic strength pH – acid having only one dissociable H\(^+\) ion from –OH group and can therefore represented

\[
\text{HL} \rightleftharpoons \text{H}^+ + \text{L}^{-1}
\]

The titration curve of the acid and the ligand deviates at about pH 3.0 and then increase up to pH 12.0. The deviation between acid curve from ligand curve for the systems showed the dissociation of H\(^+\) from OH groups of the ligands. (Table)

**Proton – ligand formation Number (nA)**

Proton – ligand formation number (n A) were calculated by Irving and Rossotti expression.

\[
nA = \gamma - (E^0 + N) \left( V_2 + V_3 \right) / (V_0 + V_1) T_0^0 L
\]

Where,

\[
V^0 = \text{Initial volume of solution (50 ml)}
\]

\[
N = \text{Normality of sodium hydroxide}
\]

\[
T_0^0 = \text{Concentration of ligand in 50 ml solution}
\]

\[
E^0 = \text{Initial concentration of free acid (HNO}_3\text{)}
\]

\[
\gamma = \text{Number of dissociable proton from ligand}
\]

\[
V_1 \text{ and } V_2 = \text{Volume of alkali consumed by acid and ligand on same pH}
\]

**Metal – ligand formation number (n)**

The deviation of (A + L +M) curve from (A +L) started at about pH 3.5. It indicate the commencement of complex formation.

Metal – Ligand formation number (n) was calculated by following expression.

\[
n = (E^0 + N) \left( V_3 - V_2 \right) / (V_0 + V_2) (T_M^0) \times nA
\]

\[
V^0 = \text{Initial volume of solution (50 ml)}
\]

\[
N = \text{Normality of sodium hydroxide}
\]

\[
T_M^0 = \text{Concentration of the metal ions}
\]

\[
nA = \text{Proton – ligand formation number}
\]

\[
E^0 = \text{Initial concentration of free acid (HNO}_3\text{)}
\]

Where, V\(_2\) and V\(_3\) – volume of NaOH consumed by ligand and metal ions at same pH.

**Metal – Ligand Formation curves**

Formation Curves were plotted between n and pH. The metal-ligand stability constants were determination by half integral method

**Half Integral Method:** The metal- ligand stability constants (log, k\(_v\) values) are calculated from formation curves. The values of n = 0.5 which corresponds to value of The values of Pk are presented in Table No.

The values of metal – ligand stability constants i.e. log k\(_v\) for all the systems were presented in tables.

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature (oC)</th>
<th>pKa</th>
<th>logK</th>
<th>(-\Delta H) (KJmol(^{-1}) At 30(^0)C)</th>
<th>(-\Delta G) (KJmol(^{-1}))</th>
<th>(-\Delta S) (KJmol(^{-1}) deg(^{-1}) At 30(^0)C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(II)Paracetamol</td>
<td>25</td>
<td>9.54</td>
<td>3.98</td>
<td>7.147</td>
<td>22.709</td>
<td>0.049</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>9.50</td>
<td>3.96</td>
<td>22.162</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>9.45</td>
<td>3.94</td>
<td>22.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(II)Paracetamol</td>
<td>25</td>
<td>9.54</td>
<td>4.01</td>
<td>10.721</td>
<td>22.880</td>
<td>0.040</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>9.50</td>
<td>3.97</td>
<td>23.032</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>9.45</td>
<td>3.94</td>
<td>23.235</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd(II)Paracetamol</td>
<td>25</td>
<td>9.54</td>
<td>4.429</td>
<td>17.86</td>
<td>25.271</td>
<td>0.025</td>
</tr>
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<td></td>
<td>30</td>
<td>9.50</td>
<td>4.428</td>
<td>25.689</td>
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<td></td>
<td>35</td>
<td>9.45</td>
<td>4.427</td>
<td>26.107</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Conclusion

The results obtained from the pH metric measurements, the values of pKa were found to decrease with increasing temperature. The values of the thermodynamic functions ΔG, ΔH and ΔS were calculated. The values of stability constants reveal that the stability constants decrease with increasing temperature, along with the pKa value.

Acknowledgement

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References

[2] IPCS INCHEM – Chemical safety information from intergovernmental Organizations, Poisons Information Monographs (PIMs), PIM 396.